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(54) Wursthüllen aus thermoplastischer Stärke und Verfahren zu deren Herstellung

(57) Die vorliegende Erfindung betrifft die Verwendung von thermoplastisch verarbeitbarer Stärke für Wursthüllen sowie ein Extrusionsverfahren zu ihrer Herstellung.

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HOECHST AKTIENGESELLSCHAFT - WERK KALLE-ALBERT

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Sausage casings made of thermoplastic starch and process for the production thereof

The present invention relates to a tubular sausage casing and to an extrusion process for the production thereof.

In sausage production, virtually only the collagen casings (= membrane fibrous casings), the cellulose hydrate casings and casings made of synthetic polymers have achieved importance. The latter generally comprise polyamide, polyethylene, polypropylene, poly(ethylene terephthalate), poly(butylene terephthalate) or poly(vinylidene chloride) copolymers. Other synthetic casings, such as casings made of protein- or acrylate-coated fabric are scarcely worthy of mention.

Collagen casings and cellulose hydrate casings have the advantage that they are produced from renewable raw materials, are biodegradable and thus can be composted. The processes for their production, however, are generally highly complex and environmentally polluting. Thus, for example, synthetic casings based on cellulose hydrate are produced by the viscose process, in which sodium hydroxide solution and carbon disulfide are used.

The casings produced from synthetic polymers can be produced simply and inexpensively by extrusion, but they are not biodegradable and must therefore be disposed of in a complex manner.

The object was therefore to provide a sausage casing which combines in itself the advantages of the known casings. It should be suitable for all sausage types, it should be producible simply and in an environmentally friendly manner from renewable raw materials and be

biodegradable.

The object has been achieved by the use of starch which can be processed like a thermoplastic.

Natural starch, such as potato starch, corn starch or cereal starch, is composed of macromolecules and is highly inhomogeneous. The macromolecules occur in the form of α-helix. On heating, the natural starch decomposes before it reaches the melting temperature. If water is added in advance, a composition which can be processed like a thermoplastic is obtained. Since water, because of its low boiling point, is not so expedient in processing terms, additives such as glycerol, ethylene glycol or propylene glycol are more suitable, since they have a higher boiling point. The proportion of these additives should be at least 5 % by weight, based on the weight of the dry starch.

Thermoplastic starch, process for the production thereof and shaped bodies produced therefrom are disclosed by WO 90/05161 and 90/10019. The applications specified were: filler or formulation aid in thermoplastics and thermosets or support material for active compounds, such as pharmaceutical active compounds, or reagents such as flocculents for waste water. It is stated that extruded films of thermoplastic starch can be laid out in a low-water environment or on a water-permeable underlay and bind water. This is said to improve the efficiency of soil irrigation in arid regions. There has been no previous indication that thermoplastic starch could be suitable for the production of sausage casings, especially those which cover a broad field of application.

The starting material used for the production of the sausage casings is thermoplastic starch which is disclosed in the said WO publications. This starch generally occurs as granules or in the form of beads. It is critical for the production of sausage casings having

optimal properties that the natural starch is converted into the amorphous state with abolition of the α-helix structure. This is successfully achieved, for example, by heating and mechanical mixing, expediently in a kneader or in a single- or twin-screw extruder. In order to achieve melting of the starch below the decomposition temperature, the known plasticizers such as water, butane-1,3-diol, glycerol, diglycerol, N,N-dimethylurea, sorbitol or citrate are used.

When water is used as plasticizer, this is used in an amount of about 15 to 25 % by weight, preferably about 17 % by weight, based in each case on the weight of the plasticized starch. The temperature should be about 100 to 130°C. When glycerol is used as plasticizer, an amount of 0.5 to 20 % by weight, preferably 8 to 16 % by weight, is sufficient, again based on the weight of the starch in each case. The temperature in this case is expediently somewhat higher. 150 to 170°C is favorable. The crystalline proportion in the thermoplastic starch should at any event be less than 5 % by weight.

In order to adapt the casings to the various sausage types, suitable substances are added to the granulated thermoplastic starch. These are in particular fibers which increase the mechanical strength. Such sausage casings are novel and are part of the present invention.

Casings for raw sausage, in addition to the thermoplastic starch, expediently contain

5 to 30 % by weight,	preferably 10 to 20 % by weight, fiber reinforcement, preferably cotton combings,
3 to 25 % by weight,	preferably 5 to 15 % by weight, protein, preferably gelatin, casein or wheat protein, and
2 to 15 % by weight,	preferably 3 to 10 % by weight, crosslinker, preferably a

dicarboxylic acid, a dialdehyde, a diisocyanate or a diepoxide.

These and also the following figures in % by weight relate to the weight of the plasticized starch (total weight of starch + plasticizer).

In order to satisfy the requirements for scalded-meat sausage and cooked-meat sausage and cooked ham, fiber reinforcement is necessary. Cotton linters, synthetic fibers or regenerated fibers (= fibers from regenerated cellulose) are particularly suitable therefor. The proportion of fiber reinforcement is generally 3 to 25 % by weight, preferably 5 to 15 % by weight.

A further quality improvement - depending on the application - may be achieved by additional synthetic polymers, preferably soft and ductile polyamides, polyesters, polyolefins, ethylene/ethylacrylate/maleic anhydride copolymers or polyvinylpyrrolidone (PVP). The polyolefins are preferably low-density polyethylenes or polypropylenes. The proportion of the synthetic polymers is expediently 5 to 50 % by weight, preferably 10 to 40 % by weight. Crosslinkers increase the water resistance. Their proportion, in the casings for scalded-meat sausage and cooked ham, is 2 to 20 % by weight, preferably 3 to 12 % by weight. Preferred crosslinkers have already been mentioned under raw sausage casings. Lubricants can facilitate extrusion. For this purpose, the animal or vegetable fats or lecithins already disclosed in the abovementioned WO 90/05161 are especially suitable. Lubricants improve the peelability and likewise the water resistance. Their proportion is generally 2 to 12 % by weight, preferably 3 to 6 % by weight.

Fiber-free, transparent casings, in addition to the thermoplastic starch, expediently contain alginate, chitosan, extrudable cellulose derivatives (preferably cellulose acetate or cellulose propionate) and/or

proteins (preferably gelatin). The proportion of additional constituents is from 5 to 70 % by weight, preferably 20 to 50 % by weight. To improve the mechanical stability and the water resistance and resistance to boiling, the abovementioned crosslinkers can additionally be present in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight. The suppleness of the stretched sausage casing can be further improved by a softener, preferably glycerol or citric ester. The proportion of the added softener is 3 to 30 % by weight, preferably 5 to 20 % by weight.

A process for the production of starch-based sausage casings is likewise subject-matter of the present invention. The process comprises molding the mixture of thermoplastic starch and the remaining constituents using an extruder, preferably a single- or twin-screw extruder and a ring die attached thereto which is heated to 100 to 140°C, preferably 105 to 120°C to give a tubular casing, inflating this and stretching it in a ratio of 1:2 to 1:10, preferably 1:3 to 1:5, based on the surface area in each case. A homogeneous melt thus forms in the extruder. During stretching by blow molding, the casing is preferably inflated using air.

In a further step, an impregnation or coating can subsequently be applied internally and/or externally. It serves in particular to improve the sausage emulsion adhesion or to increase resistance to mold.

The starch-based sausage casings exhibit all of the positive properties of cellulose hydrate casings. The impregnations or coatings known from the cellulose hydrate casings are generally also suitable for the starch casings. In particular, layers can also be applied which act as a barrier for oxygen and/or water vapour. The starch casings can be adapted by this means to all important sausage types.

Production of the thermoplastic starch

100 kg of potato starch were dried in vacuo until the water content was less than 0.3 % by weight. The starch was then mixed with 50 kg of glycerol (99 % by weight pure) in a kneader at a temperature of 160 to 190°C. To abolish the helix structure, the melt produced in this process was kept for about 2 hours at a temperature of 170°C. It was then extruded and granulated. Even after relatively long storage, the starch remained virtually completely amorphous in the granules.

Example 1

To produce a raw sausage casing having fiber reinforcement,

75.0 kg	of the abovedescribed granules (50 kg of starch + 25 kg of glycerol) were mixed with
10.0 kg	of cotton linters,
10.0 kg	of gelatin,
2.5 kg	of adipic acid and
2.5 kg	of sunflower seed oil,

extruded at 110 to 120°C and stretched longitudinally and transversely in the ratio of 1:8, based on the surface area. In this manner, a tube of caliber 60 (= 60 mm) was obtained, having a wall thickness of 90 μm.

The tube was then laid flat, wound up and then gathered together to form concertinaed casings or finished to form sections tied off at one end.

In order to test the mechanical properties of the casing, it was soaked in water and subjected to a pressure test. It did not burst until a pressure of 65 to 72 kPa (bursting pressure) was reached. The static extension at 21 kPa was 65 to 75 mm.

In order to test the applicability, the casings were

filled with salami emulsion and subjected to the usual ripening process. During ripening, the casing did not detach from the emulsion, i.e. "disconnection" of the casing did not occur. The peelability of the ripened salami was evaluated as "2" (rating scale of 1 to 6; 1 = very good peelability, 6 = no longer peelable).

Example 2

To produce a casing for scalded-meat\ and cooked-meat sausage and cooked ham,

75.0 kg	of the abovedescribed granules were mixed with
7.5 kg	of cotton linters,
20.0 kg	of a soft, supple copolyamide,
5.0 kg	of glyoxal and
7.5 kg	of lecithin.

The mixture was homogenized by kneading for about half an hour at 185°C and was then extruded through a ring die for caliber 60. By blow-molding, the tubular casing was then stretched longitudinally and transversely in the ratio of 1:6 (based on the surface area). The wall thickness of the stretched tube was 85 μm. The bursting pressure of the water-soaked casings was 72 kPa, the static extension at 21 kPa was 68 mm.

A water-soaked casing piece tied off at one end was then filled with meat sausage emulsion. The casing could be removed without difficulty from the conventionally scalded and smoked sausage.

Example 3

To produce a fiber-free, transparent sausage casing,

75.0 kg	of the abovedescribed granules were mixed with
20.0 kg	of gelatin,
10.0 kg	of chitosan

7.5 kg of glyoxal,
5.0 kg of triethyl acetylcitrate ((R)Citroflex A4) and
2.5 kg of lecithin,

processed in an extruder at 178°C to give a homogeneous melt and extruded through a ring die for caliber 75. The tubular casing was then stretched longitudinally and transversely by blow-molding in the ratio of 1:8 (based on the surface area), then laid flat and wound up. The wall thickness of the stretched casing was 108 µm. The bursting pressure of the water-soaked casing was 30 kPa. The static extension at 15 kPa was 88 to 92 mm.

Sections of the tubular casing tied off at one end were filled with "Bierwurst" emulsion. After scalding and smoking, the casing could be peeled off easily from the emulsion.

Example 4

A fiber-free casing could also be produced with starch which had been plasticized with water instead of glycerol. For this purpose,

100.0 kg of potato starch were mixed with
7.0 kg of water,
1.0 kg of sunflower seed oil and
0.5 kg of lecithin.

The mixture was melted in a kneader at 165°C and homogenized for 1 hour. The melt was then extruded and granulated.

60.0 kg of the granules thus produced were then mixed with
10.0 kg of gelatin,
10.0 kg of chitosan,
10.0 kg of glycerol,
7.5 kg of glyoxal and

5.0 kg of sunflower seed oil.

The mixture was converted into a homogeneous melt using an extruder and was extruded through a ring die for caliber 80. By blow-molding in the ratio 1:6 (based on the surface area), the tubular casing was then stretched longitudinally and transversely. The casing was then laid flat and rolled up. The wall thickness of the stretched casing was 95 μm. The bursting pressure of the water-soaked casing was 22 kPa. The static extension at 15 kPa was 95 to 100 mm.

Casing part-pieces tied off at one end were filled with long-keeping-sausage emulsion. The sausages ripened without defect and could be easily peeled.

Patent Claims

1. Use in sausage casings of starch which can be processed like a thermoplastic.

2. A thermoplastic-starch-based casing for raw sausage, which casing, apart from thermoplastic starch, contains

   5 to 30 % by weight of fiber reinforcement,
   3 to 25 % by weight of protein and
   2 to 15 % by weight of crosslinker.

3. A thermoplastic-starch-based casing for scalded-meat sausage and cooked ham which, apart from thermoplastic starch, contains 3 to 25 % by weight of a fiber reinforcement.

4. The casing as claimed in claim 3, wherein it additionally contains synthetic polymers, crosslinkers and/or lubricants.

5. The casing as claimed in claim 4, wherein the proportion of the synthetic polymers is 5 to 50 % by weight, preferably 10 to 40 % by weight, the proportion of the crosslinkers is 2 to 20 % by weight, preferably 3 to 12 % by weight and the proportion of the lubricants is 2 to 12 % by weight, preferably 3 to 6 % by weight.

6. A thermoplastic-starch-based, fiber-free, transparent sausage casing which, in addition to thermoplastic starch, contains alginate, quitosan, extrudable cellulose derivatives and/or proteins in a proportion of from 5 to 70 % by weight.

7. The casing as claimed in claim 6, wherein it contains crosslinkers in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight, and/or softeners in a proportion of from 3 to 30 % by weight, preferably 5 to 20 % by weight.

8. A process for the production of sausage casings as claimed in claims 2 to 7, which comprises molding the mixture of thermoplastic starch and the remaining constituents using an extruder and a ring die attached thereto which is heated to 100 to 140°C to give a tubular casing, then inflating this and stretching it in the ratio 1:2 to 1:10, based on the surface area in each case.

9. The process as claimed in claim 8, wherein the tubular casing is stretched in the ratio of 1:3 to 1:5, based on the surface area in each case.

10. The process as claimed in claim 8 or 9, wherein an impregnation or coating is applied internally and/or externally to the stretched sausage casings.

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Abstract:

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The present invention relates to the use for sausage casings of starch which can be processed like a thermoplastic and to an extrusion process for the production thereof.